Anodic Oxidation of Derivatives of Methane, Ethane and Propane in Aqueous Electrolytes

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Abstract*

The behavior of twelve partially oxidized hydrocarbons of the paraffin series during anodic oxidation was studied at temperatures of 25° C and 80° C using an immersed Raney platinum electrode in 5 N sulfuric acid and 5 N potassium hydroxide. Galvanostatic potential-current density curves gave information on the differences in reactivity of the individual substances; the degree of conversion was determined from potentiostatic-coulometric measurements.

With Raney platinum electrodes anodic oxidation of carboxylic acids was observed only in sulfuric acid at 80° C to give carbon dioxide and water. With sulfuric acid at 25° C and with potassium hydroxide electrolyte practically no reaction was observed. One exception was formic acid which is the only carboxylic acid that, as a reduction product of carbon dioxide, still contains a reactive hydrogen atom attached to the carbonyl-C atom. Even at room temperature, it is oxidized at a considerable rate both in sulfuric acid and potassium hydroxide solution.

At a temperature of 80° C, the polarization involved in the conversion of alcohols is generally smaller in potassium solution than in sulfuric acid. With the exception of methanol, the reaction in 5 N potassium hydroxide proceeds up to the step of carboxylic acid.

Methanol can be oxidized to carbon dioxide in alkalies as well as in acids. Oxidation of ethanol in sulfuric acid leads to complete conversion to carbon dioxide; the evaporation of acetaldehyde formed as an intermediate must be prevented.

In the case of isopropanol, the reaction proceeds only to acetone; this in turn is nearly inactive. At reasonable potentials only small current densities are observed both in alkalies and in acids even at $80^{\rm O}$ C. The oxidation of acetone probably only proceeds via its condensation products.

The polyvalent alcohols glycol and glycerol can be converted at considerable current densities both in sulfuric acid and potassium hydroxide solution even at room temperature. In acid solutions, the oxidation proceeds up to carbon dioxide.

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